Statistical Thermodynamics in Chemistry and Biology

5. Entropy and the Boltzmann distribution law

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Agenda

We will continue adding piece by piece to the puzzle...
In this chapter, we will discuss:

- Entropy: connection between entropy, multiplicity, and probability
- Boltzmann's distribution law: a first glance

What is entropy?

- Boltzmann's law:

$$S = k_B \ln W$$

- From a probability perspective, we "know":

$$S = -k_B \sum_{i=1}^{t} p_i \ln p_i$$

- The multiplicity W (e.g. for placing t types of molecules on a lattice):

$$\ln W = \ln \frac{N!}{n_1!n_2!\dots n_t!} \overset{Stirling}{\approx} N \ln N - N - \sum_{i=1}^{t} (n_i \ln n_i - n_i)$$

$$= -\sum_{i=1}^{t} n_i \ln \frac{n_i}{N} = -N \sum_{i=1}^{t} p_i \ln p_i$$

where we essentially used $\sum_{i=1}^{t} n_i = N$ in "both directions".

What is entropy?

Part 2

- To continue:

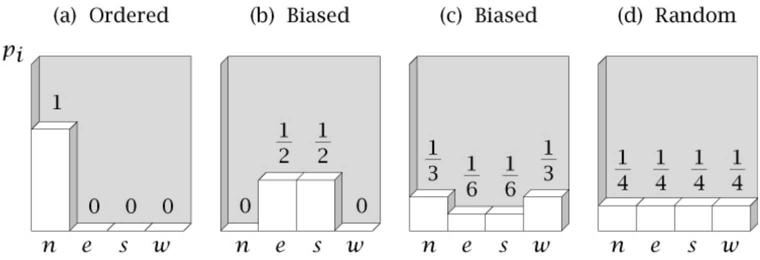
$$\ln W = -N \sum_{i=1}^{t} p_i \ln p_i \qquad \Rightarrow \qquad \frac{1}{N} \ln W = -\sum_{i=1}^{t} p_i \ln p_i = \frac{S_N}{N k_B}$$

where S_N is the entropy for N trials. The normal definition of entropy is per trial (or per particle or per mole)

$$S = \frac{S_N}{N}$$

Example 5.1: Order and disorder

Spin a pencil N times: *north*, *east*, *west*, and *south*



$$W = \frac{N!}{n_n! n_e! n_w! n_s!}$$

- Which case in the figure gives the maximum multiplicity?
- A water molecule has a dipole moment. Which dipole moment has *liquid water*? *Liquid water has on average a zero dipole moment.*

Minimization with constraints

See chapter 4, pages 66-72

- Assume that we would like to minimize a function $f(x,y)$ with the constraint $g(x,y) = 0$.
- The method of Lagrange multipliers: construct a function $h(x,y)$,

$$h(x,y) = f(x,y) - \lambda g(x,y)$$

  where λ is a Lagrange multiplier.
- Minimize $h(x,y)$ with respect to x, y and λ,

$$\frac{\partial h(x,y)}{\partial x} = 0$$

$$\frac{\partial h(x,y)}{\partial y} = 0$$

$$\frac{\partial h(x,y)}{\partial \lambda} = g(x,y) = 0$$

Maximum entropy: no (physical) constraints

- Still, the probability has to sum to 1:

$$\sum_{i=1}^{t} p_i = 1 \qquad \Rightarrow \qquad \sum_{i=1}^{t} dp_i = 0$$

- We seek the distribution $(p_1^*, p_2^*, \ldots p_t^*)$ that maximizes the entropy, S,

$$S(p_1, p_2, \ldots, p_t) = -k_B \sum_{i=1}^{t} p_i \ln p_i$$

  subject to the constraint above.

- Note the differential of S:

$$dS = \sum_{i=1}^{t} \frac{\partial S}{\partial p_i} dp_i$$

Maximum entropy: no (physical) constraints

Part 2

- Solve by the Lagrange multiplier method:

$$\sum_{i=1}^{t}\left(\frac{\partial S}{\partial p_i}-\alpha\right)dp_i=0$$

where α is the Lagrange multiplier (including also k_B).

- Has to be fulfilled for each i:

$$-1-\ln p_i^*-\alpha=0 \qquad \Rightarrow \qquad p_i^*=e^{(-1-\alpha)}$$

- To simplify:

$$p_i^*=\frac{p_i^*}{1}=\frac{p_i^*}{\sum\limits_{i=1}^{t}p_i^*}=\frac{e^{(-1-\alpha)}}{te^{(-1-\alpha)}}=\frac{1}{t}$$

- Conclusion: Even (flat) distribution

Maximum entropy: constant energy

- The total energy is constant:

$$E = \sum_{i=1}^{t} \varepsilon_i n_i \qquad \Rightarrow \qquad \frac{E}{N} = \sum_{i=1}^{t} p_i \varepsilon_i$$

- We seek the distribution that maximizes the entropy with an extra constraint: the probabilities still have to sum to 1 and the energy is E/N is constant:

$$\sum_{i=1}^{t} dp_i = 0 \; ; \qquad \sum_{i=1}^{t} \varepsilon_i dp_i = 0$$

- Solve by the Lagrange multiplier method:

$$\sum_{i=1}^{t} \left(\frac{\partial S}{\partial p_i} - \alpha - \beta\varepsilon_i \right) dp_i = 0$$

- Langrange multipliers give (analogously to the previous example):

$$-1 - \ln p_i^* - \alpha - \beta\varepsilon_i = 0 \qquad \Rightarrow \qquad p_i^* = e^{(-1-\alpha-\beta\varepsilon_i)}$$

Maximum entropy: constant energy

Part 2

- Same approach again:

$$p_i^* = \frac{p_i^*}{1} = \frac{p_i^*}{\sum_{i=1}^{t} p_i^*} = \frac{e^{(-1-\alpha)}e^{-\beta\varepsilon_i}}{\sum_{i=1}^{t} e^{(-1-\alpha)}e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=1}^{t} e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{q}$$

- The Boltzmann distribution law

$$p_i^* = \frac{e^{-\beta\varepsilon_i}}{q}$$

- q is the partition function

$$q = \sum_{i=1}^{t} e^{-\beta\varepsilon_i}$$

  which is a very central concept in statistical thermodynamics.
- The Lagrange multiplier, β, is at this stage not determined.

Summary

- Defined entropy from Boltzmann's law.
- Derived the Boltzmann distribution law for two cases.
- The partition function is defined.